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# Exchange energy gradients with respect to atomic positions and cell parameters within the Hartree-Fock Γ-point approximation

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Recently, linear scaling construction of the periodic exact Hartree-Fock exchange matrix within the Γ-point approximation has been introduced [J. Chem. Phys. **122**, 124105 (2005)]. In this article, a formalism for evaluation of analytical Hartree-Fock exchange energy gradients with respect to atomic positions and cell parameters at the Γ-point approximation is presented. While the evaluation of exchange gradients with respect to atomic positions is similar to those in the gas phase limit, the gradients with respect to cell parameters involve the accumulation of atomic gradients multiplied by appropriate factors and a modified electron repulsion integral (ERI). This latter integral arises from use of the minimum image convention in the definition of the Γ-point Hartree-Fock approximation. We demonstrate how this new ERI can be computed with the help of a modified vertical recurrence relation in the frame of the Obara-Saika and Head-Gordon-Pople algorithm. As an illustration, the analytical gradients have been used in conjunction with the QUICCA algorithm [K. Németh and M. Challacombe, J. Chem. Phys. **121**, 2877 (2004)] to optimize periodic systems at the Hartree-Fock level of theory.



## I. INTRODUCTION

In preceding papers, we have developed linear scaling quantum chemical methods for construction of the periodic Coulomb, exchange-correlation,[1] and the exact Hartree-Fock exchange[2] matrices within the Γ-point approximation. In this paper, the implementation of the Hartree-Fock exchange gradients with respect to atomic positions and cell parameters at the Γ point is presented. The formalism for the evaluation of the Coulomb and exchange-correlation energy cell gradients will be presented in a companion paper.[3]

The Hartree-Fock approximation is often a fast, first approximation and also a starting point for correlated wave function methods. Also, the hybrid Hartree-Fock/density functional theory (HF/DFT) model chemistries are an important next step in accuracy beyond the generalized gradient approximation.[4–7] Together with linear scaling methods for computing the density matrix,[8,9] these advances provide a framework for the application of both HF and HF/DFT models to large condensed phase systems, surfaces, and wires.

While the Γ-point approximation uses only the $\mathbf{k}=0$ point to sample the Brillouin zone, it does, however, converge to the **k**-space integration limit, in the worst case with the inverse cell volume (see, for example, Refs. 10 and 11). The convergence of the Γ-point approximation to the corresponding **k**-space limit was recently demonstrated by us for DFT,[1] HF, and hybrid HF/DFT (Ref. 2) level of theories. The Γ-point approach opens the capabilities of studying very large complex and disordered systems such as liquids, low concentration defects, adsorption of large molecule on surfaces, etc., where conventional methods of sampling the Brillouin zone may become computationally too demanding, and where the Γ-point approximation is well justified.

Finding crystal structures of condensed systems can be formulated as a minimization of the total energy with respect to atomic coordinates and cell vectors. The problem is then minimization of the total energy with $L$ degrees of freedom, where $L=3N_{\mathrm{atm}}+3$, $N_{\mathrm{atm}}$ is the number of atoms, $3N_{\mathrm{atm}}-3$ is the number of independent coordinates after the elimination of translation, and the number of independent cell vector elements after the elimination of cell rotations is 6. This minimization can be achieved with the help of an efficient optimizer[12–14] and the knowledge of the gradients with respect to atomic positions and cell parameters.

The first implementation of the Hartree-Fock cell gradients based on Gaussian-type atomic orbitals (GTAO), was for one dimensional periodic systems.[15,16] Other groups have also described such implementations for one[17,18] and two[19] dimensions. The analytical cell gradient method of density functional theory using GTAO for one dimensional (1D) extended systems was implemented by Hirata and Iwata.[20] The three dimensional case has been implemented by Kudin and Scuseria.[21,22] Their approach for the Coulomb problem is based on the direct space fast multipole method. We should also mention the plane-wave local density functional (LDF) formulation by Nielsen and Martin[23] and the LDF-LCAO (linear combination of atomic orbitals) derivation of the cell gradients by Feibelman.[24] Recently Doll *et al.*[25] presented implementation of the Hartree-Fock cell gradients[26] in the CRYSTAL03 (Ref. 27) package for three dimensional systems. Their code is based on GTAO and the summation of the Coulomb energy is performed using an Ewald method,[28]

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which is a combination of direct and reciprocal cell summations. For an efficient truncation of the three infinite summations of the exchange series, the CRYSTAL03 program uses, in the first hand, the decay between local basis function products and, in the second, the fact that elements of the density matrix of an insulator decay exponentially with interatomic separation. The strategy to compute the analytical Hartree-Fock gradients for periodic system, in the frame of the CRYSTAL03 package, has been presented by Doll *et al.*[29] and Doll.[30] Their implementation is based on the Hermite Gaussian-type functions in the context of the McMurchie-Davidson algorithm.[31]

The HF-MIC (minimum image convention) model is a translationally invariant definition of Γ-point Hartree-Fock exchange, which correctly approaches the **k**-space integration value in the limit of a large cell. This is accomplished through introducing a MIC into the exchange kernel at the level of primitive two-electron integrals.

As shown later, evaluation of the atomic exchange energy gradients within the Γ-point approximation does not lead to special difficulties. The implementation requires evaluation of the derivative of the electron repulsion integrals (ERIs) with respect to atomic positions and, except for applying the MIC at the primitive level, it is similar to what has been done in the past for molecular calculations.[32–36] However, difficulties arise when derivative of ERI's are taken with respect to cell parameters. In this case the derivative provides, after some manipulation, a new type of integral that arises due to the use of the MIC in the Γ-point approximation. This integral can be evaluated with the help of a modified recurrence relation (RR) similar to the vertical recurrence relation (VRR) introduced by Obara and Saika (OS).[32]

The remainder of this paper is organized as follows: In Sec. II, we introduce the formalism and discuss the implementation of the Hartree-Fock exchange energy gradients with respect to atomic positions and cell parameters at the Γ-point approximation. Full optimization of several periodic systems are given in Sec. III as an illustration of the formalism. Finally, in Sec. IV we summarize our results.

## II. HARTREE-FOCK EXCHANGE ENERGY

The cell is given by the three vectors **a**, **b**, and **c**. Then $M$ is the $3\times3$ matrix composed of the cell vectors

$$M(\mathbf{a},\mathbf{b},\mathbf{c}).$$

The position of a cell is $\mathbf{R}(\mathbf{n})=M\mathbf{n}$, with $\mathbf{n}=(n_a,n_b,n_c)$ a vector of integers. The position of atom $A$ in the cell $\mathbf{R}(\mathbf{n})$ is $\mathbf{A}=M(\mathbf{f}_A+\mathbf{n})$, with $\mathbf{f}_A=(f_{Aa},f_{Ab},f_{Ac})$ the fractional coordinates of atom $A$ in the central cell.

An unnormalized Cartesian Gaussian-type function (CGTF) centered on atom $A$ is

$$\phi_a(\mathbf{r}) = (x-A_x)^{a_x}(y-A_y)^{a_y}(z-A_z)^{a_z}e^{-\zeta_a(\mathbf{r}-\mathbf{A})^2},$$

where the triad $a=(a_x,a_y,a_z)$ sets the angular symmetry and the exponent $\zeta_a$ is chosen to describe a particular length scale. Gaussian basis functions are often contracted to approximate atomic eigenfunctions.

The Hartree-Fock exchange energy within the MIC Γ-point approximation[2] is given by

$$E^x(\mathbf{f}_A,\mathbf{f}_B,\ldots,M) = -\tfrac{1}{4}\sum_{\substack{\mathbf{mn}\\ abcd}} P_{ab}P_{cd}(ac^{\mathbf{m}}|bd^{\mathbf{n}}),$$

where the indices **mn** run over the direct cell vectors, *abcd* over the basis functions, $P=P(\mathbf{f}_A,\mathbf{f}_B,\ldots,M)$ is the density matrix, and the ERIs are written in the Mulliken notation and computed with the MIC as discussed in the following.

The minimum image convention is applied in the so-called $K^4$ loop (where $K$ is the degree of contraction) to the interaction vector $\mathbf{P}-\mathbf{Q}$ during evaluation of the ERIs and is repeated here for clarity,

$$\mathbf{PQ} = M(\mathbf{f}_{PQ} - [\mathbf{f}_{PQ} - \varepsilon\ \mathrm{sgn}(\mathbf{f}_{PQ})]), \tag{1}$$

where $\mathbf{f}_{PQ}=M^{-1}(\mathbf{P}-\mathbf{Q})$, $\mathbf{P}=(\zeta_a\mathbf{A}+\zeta_c\mathbf{C})/(\zeta_a+\zeta_c)$, $\mathbf{Q}=(\zeta_b\mathbf{B}+\zeta_d\mathbf{D})/(\zeta_b+\zeta_d)$, $\varepsilon\approx10^{-15}$ is required to yield a consistent wrapping when distributions lie at the cell boundary and $[\cdot]$ is the nearest integer function defined as $[x]:=n$ with $x\in\mathbb{R}$, $n\in\mathbb{Z}$ and $|x-n|<1/2$. Note that $\mathbf{PQ}=\mathbf{P}-\mathbf{Q}$ if and only if $[\mathbf{f}_{PQ}-\varepsilon\ \mathrm{sgn}(\mathbf{f}_{PQ})]=0$. In the following sections the notation **PQ** will always refer to Eq. (1).

As an example, the MIC integral over $s$-type CGTF is given by

$$(00|00)^{(m)} = \left(\frac{\rho}{\pi}\right)^{1/2}\left(\frac{\pi}{\zeta}\right)^{3/2}\left(\frac{\pi}{\eta}\right)^{3/2}\exp\left(-\frac{\zeta_a\zeta_c}{\zeta}AC^2\right)\times\exp\left(-\frac{\zeta_b\zeta_d}{\eta}BD^2\right)F_m(\rho PQ^2),$$

where $\zeta=\zeta_a+\zeta_c$, $\eta=\zeta_b+\zeta_d$, $\rho=\zeta\eta/(\zeta+\eta)$, $AC^2=|\mathbf{A}-\mathbf{C}|^2$, $BD^2=|\mathbf{B}-\mathbf{D}|^2$, $PQ^2=|\mathbf{PQ}|^2$ is given by Eq. (1), $m\in\mathbb{Z}^*$ plays the same role as in the OS algorithm (the integrals with $m=0$ are true ERIs, while integrals with $m>0$ are auxiliary integrals), and $F_m(x)=\int_0^1 t^{2m}\exp(-xt^2)dt$ is the reduced incomplete gamma function.[37]

### A. Gradients with respect to atomic positions

The exchange energy gradient with respect to the fractional coordinate $f_{Gj}$, at constant $P$, can be obtained through the linear transform

$$\left.\frac{\partial E^x}{\partial f_{Gj}}\right|_P = \sum_{i=x,y,z} M_{ij}\left.\frac{\partial E^x}{\partial G_i}\right|_P,$$

where $\partial E^x/\partial G_i|_P$ is the exchange energy gradient with respect to atomic position given by

$$\left.\frac{\partial E^x}{\partial G_i}\right|_P = -\tfrac{1}{4}\sum_{\substack{\mathbf{mn}\\ abcd}} P_{ab}P_{cd}\frac{\partial(ac^{\mathbf{m}}|bd^{\mathbf{n}})}{\partial G_i}, \tag{2}$$

where the indices *abcd* and **mn** run over the basis functions and the Bravais vectors, respectively.

Starting with $\partial PQ_k/\partial A_i=\delta_{ik}\zeta_a/(\zeta_a+\zeta_c)$ it is then possible to see, after further manipulations, that the evaluation of the derivative $\partial(ac^{\mathbf{m}}|bd^{\mathbf{n}})/\partial G_i$ is analogous to its correspondent gas phase limit [except for the application of the MIC, Eq. (1), in the $K^4$ loop]. Therefore, the evaluation of the atomic exchange energy gradients at the Γ point can be carried out

with standard RR's, with addition of the MIC, and does not need to be addressed in more detail. As in the gas phase case, translational invariance[38] can likewise be used to reduce the computational cost of atomic gradient calculation.

### B. Gradients with respect to cell parameters

The Γ-point MIC exchange energy gradients with respect to cell parameters are given by

$$\left.\frac{\partial E^x}{\partial M_{ij}}\right|_P = -\frac{1}{4}\sum_{\substack{\mathbf{mn}\\abcd}} P_{ab}P_{cd}\frac{\partial(ac^{\mathbf{m}}|bd^{\mathbf{n}})}{\partial M_{ij}}, \tag{3}$$

where the summations are the same as in (2). The derivative of the integrals $(ac^{\mathbf{m}}|bd^{\mathbf{n}})$, with respect to cell parameters $M_{ij}$, can be further decomposed as

$$\begin{aligned}\frac{\partial(ac^{\mathbf{m}}|bd^{\mathbf{n}})}{\partial M_{ij}} &= (f_{Aj}-(f_{Dj}+n_j))\frac{\partial(ac^{\mathbf{m}}|bd^{\mathbf{m}})}{\partial A_i}\\ &+(f_{Cj}+m_j-(f_{Dj}+n_j))\frac{\partial(ac^{\mathbf{m}}|bd^{\mathbf{n}})}{\partial C_i}\\ &+(f_{Bj}-(f_{Dj}+n_j))\frac{\partial(ac^{\mathbf{m}}|bd^{\mathbf{n}})}{\partial B_i}+[ac^{\mathbf{m}}|bd^{\mathbf{m}}]_{ij},\end{aligned} \tag{4}$$

where we have used translational invariance.[38] The integral derivatives $\partial(ac^{\mathbf{m}}|bd^{\mathbf{n}})/\partial A_i$, $\partial(ac^{\mathbf{m}}|bd^{\mathbf{n}})/\partial B_i$, and $\partial(ac^{\mathbf{m}}|bd^{\mathbf{n}})/\partial C_i$ are just the atomic gradients. The extra term $[ac^{\mathbf{m}}|bd^{\mathbf{n}}]_{ij}$, which is not present in previous derivations,[19,22,25] has its origin in the derivative of the minimum image convention used in our Γ-point approximation. This can be seen by taking the derivative of Eq. (1) with respect to $M_{ij}$ as

$$\frac{\partial PQ_k}{\partial M_{ij}} = \delta_{ik}(f_{PQj}-[f_{PQj}-\varepsilon\ \mathrm{sgn}(f_{PQj})]),$$

while the rightmost term $f_{PQj}$ leads, after rearrangement, to a contribution of the weighted gradients, and the second term $[f_{PQj}-\varepsilon\ \mathrm{sgn}(f_{PQj})]$ gives extra contributions which can be collected into a new integral, the so-called $[ac^{\mathbf{m}}|bd^{\mathbf{n}}]_{ij}$.

### C. Strategy for the evaluation of $[ac|bd]_{ij}$

The integral $[ac|bd]_{ij}$ can be divided into a product of an $i$ and a $j$ part as

$$[ac|bd]_{ij} = 2\rho[f_{PQj}-\varepsilon\ \mathrm{sgn}(f_{PQj})][ac|bd]_i,$$

with $\rho$ as defined previously in Sec. II. This separation reduces the computational work in the $K^4$ loop substantially. In the following, we present a simple approach for the evaluation of the integral $[ac|bd]_{ij}$ in the spirit of the Obara-Saika[32] and Head-Gordon–Pole[33] (OS-HGP) algorithm. Generation of the two-electron integrals is broken up into two main steps: First, a set of two-electron integrals with $c=d=0$ is generated from the reduced incomplete gamma function[37] by means of a modified version of the OS-VRR. Finally, the Cartesian powers between orbitals of the same electron are transferred using the simple two term horizontal recurrence relation (HRR).[33] For the evaluation of the integral $[e0|f0]_i=[e0|f0]_i^{(0)}$, we have derived a six-term MIC-VRR similar to the one given by Obara and Saika,

$$\begin{aligned}[a+1_k0|b0]_i^{(m)} &= PA_k[a0|b0]_i^{(m)}\\ &+\delta_{ik}\frac{1}{2\zeta}(a0|b0)^{(m+1)}-\frac{\rho}{\zeta}PQ_k[a0|b0]_i^{(m+1)}\\ &+\frac{b_k}{2(\zeta+\eta)}[a0|b-1_k0]_i^{(m+1)}+\frac{a_k}{2\zeta}\\ &\times\left\{[a-1_k0|b0]_i^{(m)}-\frac{\rho}{\zeta}[a-1_k0|b0]_i^{(m+1)}\right\},\end{aligned} \tag{5}$$

where $PA_k=P_k-A_k$, $PQ_k$ is given by Eq. (1), and $a_k$ and $b_k$ are the $k$th components of the angular symmetry indices of $\phi_a$ and $\phi_b$, respectively. Similar relations may be written down for incrementing angular momentum on any other centers by simple substitutions. The auxiliary integral, $(a0|b0)^{(m+1)}$, is a by-product of the OS-HGP scheme during the evaluation of the gradients $\partial(ac|bd)/\partial G_i$. The use of the above MIC-VRR requires the explicit evaluation of the auxiliary integral over $s$ functions $[00|00]_i^{(m)}$, which is simply

$$[00|00]_i^{(m)} = PQ_i(00|00)^{(m+1)}.$$

The horizontal recurrence relation[33] can be applied to $[a+c0|b+d0]_{ij}$ to give finally the target integral $[ac|bd]_{ij}$. The HRR shifts a unit of angular momentum from the first to the second center, i.e.,

$$[ac+1_k|bd]_{ij} = [a+1_kc|bd]_{ij}+AC_k[ac|bd]_{ij}, \tag{6}$$

where $AC_k=A_k-C_k$. An important feature of the HRR is that the constant in the second right hand term involves only the atomic centers and can be applied outside the contraction loops (i.e., $K^0$). As the evaluation of the gradients $\partial(ac|bd)/\partial G_i$ and the integral $[ac|bd]_{ij}$ share the same incomplete gamma functions $F_m(x)$ and some intermediate integrals, it is advantageous to combine the two algorithms together.

Let us now summarize the proposed algorithm for evaluating the ERI derivatives with respect to cell parameters within our Γ-point approximation: The $F_m(x)$'s are first evaluated through well known methods,[31,32] the OS-VRR and the MIC-VRR Eq. (5) are used together to generate the intermediate integrals $(e0|f0)$ and $[e0|f0]_{ij}$. The desired ERIs are then computed with the help of the HRR Eq. (6), accumulated with the weighted gradients, Eq. (4), and digested with the corresponding density matrix elements, Eq. (3), to yield, finally, the Hartree-Fock exchange contribution to the cell gradients.

## III. NUMERICAL EXAMPLES

All developments were implemented in the MONDOSCF (Ref. 39) suite of linear scaling quantum chemistry programs. The code was compiled using the HP FORTRAN compiler F95 v5.5A (Ref. 40) and the -04 option and the Compaq C compiler CC v6.5 (Ref. 41) and the -01 flag. The parallel ONX algorithm[42] for computing the Γ-point exchange matrix has been modified to compute the atomic and cell gradients.

TABLE I. Analytical Hartree-Fock atomic and cell gradients for $(HF)_6$ and $(MgO)_{32}$ with different thresholds at the RHF-MIC/6-31G and RHF-MIC/8-61G(Mg)/8-51G(O) levels of theories, respectively. Comparisons are made to numerical atomic and cell gradients obtained with the VERYTIGHT threshold. Gradients are in a.u.

| | $(HF)_6$ | | $(MgO)_{32}$ | |
|---|---|---|---|---|
| Threshold | Atomic[a] | Cell[b] | Atomic[c] | Cell[b] |
| TIGHT | −0.047 916 | −0.024 155 | −0.092 434 | −0.128 109 |
| VERYTIGHT | −0.047 941 | −0.024 230 | −0.092 436 | −0.128 074 |
| Numerical | −0.047 941 | −0.024 230 | −0.092 435 | −0.128 089 |

[a]Gradient on the F atom along the periodic axis.
[b]Component $\partial E/\partial a_x$.
[c]Gradient on the displaced Mg atom along the $x$ axis.

Geometry optimizations have been carried out using the QUICCA algorithm recently implemented by Németh and Challacombe[12,14] in MONDOSCF. All calculations were carried out on a cluster of 256 4-CPU HP/Compaq Alphaserver ES45s with the Quadrics QsNet High Speed Interconnect.

The TIGHT and VERYTIGHT levels of numerical accuracies have been used throughout this work. Thresholds that define the TIGHT (VERYTIGHT) accuracy level include a matrix threshold $\tau=10^{-6}(10^{-7})$, as well as other numerical thresholds detailed in Ref. 1, which deliver at least 8 (10) digits of relative accuracy in the total energy and 4 (5) digits of absolute accuracy in the forces.

In order to demonstrate the capabilities of our implementation of the Hartree-Fock exchange energy atomic and cell gradients, we present in this section full optimization studies of 1D and three dimensional (3D) periodic systems without any cell or atomic position symmetry constraint. Our first benchmark case is a linear chain of HF molecules the second is urea, a purely organic compound. The third benchmark system is MgO. These two latter systems have been recently optimized at the Hartree-Fock level of theory by Doll *et al.*[25]

In order to show the accuracy of the Hartree-Fock Γ-point gradients, we present in Table I the analytical atomic and cell gradients for a linear $(HF)_6$ chain and a 3D $(MgO)_{32}$ with different thresholds at the RHF-MIC/6-31G and RHF-MIC/8-61G(Mg)/8-51G(O) levels of theories, respectively. These gradients were generated by a slight deformation of the equilibrium geometries. For HF the bond length and cell parameter were $d=0.9$ Å and $a_0=2.4$ Å, respectively. For MgO, the cell parameter was $a_0=4.1$ Å and a Mg atom was moved by 0.2 Å parallel to the $x$ direction. Comparisons are made to numerical atomic and cell gradients obtained with the VERYTIGHT threshold, 21 energy points, and a sixth degree polynomial fit.

Table II shows the progression of the cell parameters $a_0$, bond lengths $d$, and total energies $E$ computed for linear $(HF)_n$ chains at the Γ-point Hartree-Fock with the split-valence 6-31G basis set. Comparisons are made to final cell parameter and bond length values obtained with 32 $k$ points in the first Brillouin zone at the RHF/6-31G level of theory.[18] We have also performed a high quality geometry optimization with the CRYSTAL03 (Ref. 27) package.

In order to analyze the convergence of the Γ-point energy to the **k**-space limit we have performed single point calculations for the $(HF)_n$ chains with cell parameter $a_0=2.4745$ Å and bond length $d=0.9453$ Å. Figure 1 shows the convergence of the Γ-point relative energy, with and without the MIC, for the $(HF)_n$ chains with an increasing cell length. The logarithm absolute error in the atomic and cell gradients is also shown in Fig. 1. These gradients were generated by a slight contraction (0.01 Å) of the bond length. The calculations with the MIC show an exponential convergence of the total energy and gradients. However, a naive implementation of the Γ-point exact exchange, i.e., without the MIC, leads to a convergence of the total energy inversely proportional to the system size, as can be seen in Fig. 2. By analogy, the behavior of the convergence of the total energy without the MIC is expected to be inversely proportional to the volume of the cell for 3D periodic systems.

We have performed full optimization of 3D urea supercells without any symmetry constraint on the cell or the atomic positions. Table III shows the cell parameters, bond lengths, bond angles, dihedral angles, and total energies for

TABLE II. Progression of the Hartree-Fock Γ-point cell parameter $a_0$, bond length $d$, and total energy $E$ for $(HF)_n$ chains using the periodic RHF-MIC/6-31G level of theory and the TIGHT thresholds. Bond lengths and cell parameters are in Å and energies in a.u.

| | $n$ | $a_0$ | $d$ | $E/n$ |
|---|---|---|---|---|
| MONDOSCF[a] | 1 | 4.5449 | 0.9201 | −99.985 278 9 |
| | 2 | 2.7960 | 0.9257 | −99.995 804 4 |
| | 4 | 2.4838 | 0.9440 | −100.002 065 |
| | 6 | 2.4746 | 0.9453 | −100.002 213 |
| | 8 | 2.4745 | 0.9453 | −100.002 217 |
| | 10 | 2.4745 | 0.9453 | −100.002 217 |
| POLOPT[b] | 1 | 2.4742 | 0.9452 | ⋯ |
| CRYSTAL03[c] | 1 | 2.4751 | 0.9451 | −100.002 205 |

[a]Γ point.
[b]32 $k$ points taken from Ref. 18.
[c]32 $k$ points, ITOL: 10 12 10 16 16 and $\Delta E=10^{-12}$.

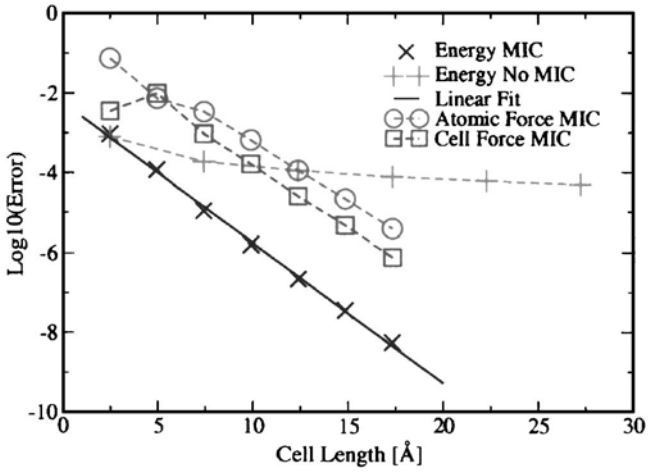


FIG. 1. Convergence of the Γ-point relative energy, with and without the MIC, for the $(HF)_n$ chains with an increasing cell length. The cell parameter $a_0=2.4745$ Å and bond length $d=0.9453$ Å were held fixed. Also shown is the absolute convergence of the atomic and cell forces for a slightly contracted bond length (see text for more detail). Calculations were performed at the RHF-MIC/6-31G level of theory with the TIGHT thresholds.

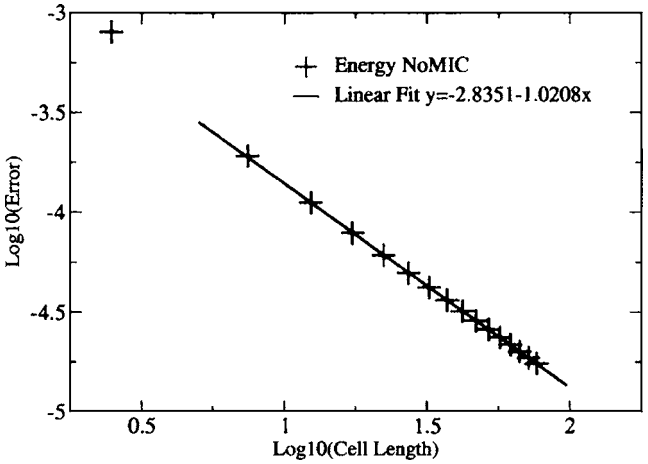


FIG. 2. Convergence of the Γ-point relative energy without the MIC for the $(HF)_n$ chains ($n$ ranges from 1 to 31) with respect to cell length. The cell parameter $a_0$=2.4745 Å and bond length $d$=0.9453 Å were held fixed. Calculations were performed at the RHF-MIC/6-31G level of theory and the TIGHT thresholds.

$(urea)_n$ supercells at the Γ-point RHF-MIC/6-21G* level of theory. The basis set used is the same as in Ref. 43. For the sake of comparison, we also present fully relaxed atomic and cell parameters for urea obtained by Civalleri[44] with the CRYSTAL03 package (last column of Table III), using a 2 ×2×2 $k$-point integration grid. While the atomic and cell parameters for urea agree perfectly between the $k$-space integration and the Γ-point approximation, the energies do not. The reason for this disagreement can be found in the different atomic basis set used. CRYSTAL03 uses spherical harmonics $d$ shells consisting of five atomic orbitals while MONDOSCF employs pure Cartesian basis functions, i.e., six atomic orbitals per Cartesian $d$ shells. To see this effect in a more quantitative way, we have performed gas phase geometry optimizations [using the GAMESS (Ref. 45) package] at the RHF/6-21G* level of theory of a single urea molecule with both spherical and Cartesian basis functions. The difference in the bond lengths and angles of the two basis sets is not more than 0.001 Å and 0.1°, respectively, but the difference in the energy is much more significant and is about 8 $\times 10^{-3}$ a.u. By inspection of the total energies in Table III, we can see that the difference in energy of the two different basis sets is of the same order ($\sim 10^{-2}$ a.u.) as that observed for the gas phase calculations. We conclude that the differences observed for the energy of urea are mainly due to the different basis set used by CRYSTAL03 and MONDOSCF.

TABLE III. Progression of the Hartree-Fock Γ-point cell parameters, bond length, bond angles, dihedral angles, and total energy for $(urea)_n$ using the periodic RHF-MIC/6-21G* level of theory and the TIGHT thresholds. Lengths, angles, and energies are in Å, °, a.u., respectively.

| | MONDOSCF[a] | | CRYSTAL03[b] |
|---|---|---|---|
| $n$ | 16 | 54 | 2 |
| $a_0$ | 5.630 | 5.636 | 5.652 |
| $c_0$ | 4.660 | 4.649 | 4.678 |
| $E/n$ | −223.853 403 | −223.853 869 | −223.842 647 |
| | | Bond lengths | |
| CO | 1.246 | 1.246 | 1.243 |
| CN | 1.334 | 1.334 | 1.333 |
| $NH_1$ | 0.999 | 0.998 | 0.997 |
| $NH_2$ | 0.998 | 0.998 | 0.996 |
| | | Bond angles | |
| OCN | 121.7 | 121.7 | 121.7 |
| $CNH_1$ | 119.5 | 119.6 | 119.3 |
| $CNH_2$ | 120.6 | 120.5 | 120.6 |
| | | Dihedral angles | |
| $OCNH_1$ | 0.0 | 0.0 | 0.0 |
| $OCNH_2$ | 180.0 | 180.0 | 180.0 |
| $NCNH_1$ | 180.0 | 180.0 | 180.0 |

[a]Γ point.
[b]2×2×2 $k$ points.

Table IV shows the progression of the cell parameters, total energies, and fractional coordinates of oxygen computed for various MgO supercells at the Γ-point RHF-MIC level of theory using the 8-61G basis set for magnesium and the 8-51G basis set for oxygen. The basis sets were specially optimized for MgO by Causà *et al.*:[46] and were obtained from Ref. 47. The cubic cell coordinates used for this system are given in Ref. 48. For comparison, we report the optimized cell parameter of cubic MgO obtained with CRYSTAL03 and a 8×8×8 $k$-point integration grid. The smallest system $(MgO)_4$ shows a large discrepancy of the cell parameter, energy, and fractional coordinate of the oxygen with respect to its **k**-space integration counterpart. The larger systems give perfect cell parameter, fractional coordinate of the oxygen, and the energy systematically converges with system size.

In Table V, we present the progression of the average of the norm of the atomic gradients for the $(MgO)_n$ systems with a cell parameter of $a_0$=4.2 Å. Note that the gradients with respect to atomic positions sum to zero within the ac-

TABLE IV. Progression of the Hartree-Fock Γ-point cell parameter $a_0$, total energy $E$, and fractional coordinate of the oxygen $f_O$ in the primitive cell for $(MgO)_n$ using the periodic RHF-MIC/8-61G/8-51G level of theory and the TIGHT thresholds. Cell parameters and energies are in Å and a.u., respectively.

| | $n$ | $a_0$ | $E/n$ | $f_O$ |
|---|---|---|---|---|
| MONDOSCF[a] | 4 | 4.365 | −274.616 533 | 0.4882 |
| | 32 | 4.192 | −274.664 119 | 0.5000 |
| | 108 | 4.192 | −274.664 299 | 0.5000 |
| CRYSTAL03[b] | 1 | 4.192 | −274.664 239 | 1/2 |

[a]Γ point.
[b]8×8×8 $k$ points.

TABLE V. Progression of the Hartree-Fock Γ-point average norm of the gradients on the Mg and O atoms for $(MgO)_n$ using the periodic RHF-MIC/8-61G/8-51G level of theory and the TIGHT thresholds. Gradients are in a.u.

| $n$ | Mg | O |
|---|---|---|
| 4 | 0.013 060 9 | 0.024 878 9 |
| 32 | 0.000 026 8 | 0.000 043 9 |
| 108 | 0.000 000 4 | 0.000 000 4 |

curacy requested. While the smallest system, $(MgO)_4$, gives large unphysical gradients which reflects the use of a too small cell for a Γ-point calculation, the larger systems provide gradients which are below the accuracy targeted by the TIGHT thresholds (i.e., an absolute error of $10^{-4}$ a.u. in the forces). These unphysical gradients observed for the $(MgO)_4$ system are responsible for breaking the symmetry of the cell (see the fractional coordinate Table IV).

## IV. CONCLUSIONS

In a previous paper, construction of the periodic exact Hartree-Fock exchange matrix within the Γ-point approximation was introduced. In this article, the formalism for the evaluation of the analytical Hartree-Fock exchange gradients with respect to atomic positions and cell parameters at the Γ-point approximation for Cartesian Gaussian-type basis functions was presented and implemented in the MONDOSCF package. While the evaluation of the exchange gradients with respect to atomic positions is similar to their gas phase limit, the exchange gradients with respect to cell parameters require the accumulation of the gradients acting on atoms multiplied by some appropriate factors and a modified ERI. The latter ERI arises from the use of the minimum image convention. We demonstrated how this new ERI can be computed with the help of a modified VRR in the frame of the Obara-Saika and Head-Gordon-Pople algorithms. This new VRR can be easily inserted in existing codes using the OS-HGP approach to compute first derivatives with respect to atomic displacement.

As an illustration, the analytical gradients and cell gradients have been used in conjunction with the QUICCA algorithm to optimize a few periodic systems at the Hartree-Fock level of theory.

For the $(HF)_n$ systems, the convergence of the HF-MIC Γ-point energy and atomic and cell gradients with respect to cell length has been explicitly shown to be exponential in the cell size (see Fig. 1). A fast convergence of the total energy and geometrical parameters has also been observed for 3D systems $(MgO)_n$ and $(urea)_n$. We believe that, for insulators, the convergence of the HF-MIC Γ-point total energy and geometrical parameters to the supercell limit is exponential with respect to cell volume. We have also shown, for the $(HF)_n$ systems, that a naive implementation of the Γ-point exact exchange, i.e., without the minimum image convention leads to a convergence of the total energy inversely proportional to the system size. For 3D periodic systems, we suggest without proof that the convergence of the total energy without the MIC scales inversely with the cell volume.

Convergence of bond lengths, bond angles, dihedral angles, and cell parameters within the HF-MIC Γ-point supercell approach and under full relaxation with no symmetry to the converged large cell Γ-point approximation has been demonstrated for 1D and 3D systems to better than three digits.

Although convergence of the HF-MIC Γ-point total energy to its **k**-space integration counterpart with respect to cell size is relatively slow, the convergence of the geometrical parameters (cell and atomic positions) requires much smaller cells. Thus, we could show that a relative accuracy better than three digits can be already achieved with cubic cells of about 600 $Å^3$.

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